Synthetic talc as a solid base catalyst for condensation of aldehydes and ketones

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Abstract

Magnesium organo silicates (MOSs; synthetic talc) as such and with amine surface functionalities were synthesized by sol–gel method under non-hydrothermal conditions and characterized by spectroscopic techniques. The synthesized talc samples were observed to be thermally stable up to 200 °C in nitrogen atmosphere and used as catalysts for condensation of aldehydes and ketones. Application of synthetic talc as a solid base catalyst for condensation of aldehydes and ketones is being reported for the first time. The effect of solvent, solvent to reactant molar ratio, amount of catalyst and temperature was studied in detail for self-condensation of propanal. High conversion (86%) of propanal with 95% selectivity of 2-methylpentenal was achieved using dimethyl sulphoxide as a solvent. The kinetic study was carried out for the condensation of propanal catalyzed by amine functionalized MOS under optimum reaction conditions. Catalyst was re-used without significant loss in activity up to three cycles.
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1. Introduction

Inorganic–organic hybrid materials are of interest because they provide an ordered array of organic moieties within a stable inorganic matrix. The organic moieties tailored on inorganic components have allowed for a variety of applications such as catalysts for organic transformations, for ion exchange, and construction of nanoscale assemblies [1,2]. Talc, uncharged member of 2:1 trioctahedral magnesium phyllosilicate series has a structure of $Si_8Mg_6O_{20}(OH)_4$. Talc consists of 0.96-nm thick layers constructed from a central sheet of octahedrally coordinated magnesium oxide/hydroxide chains (brucite sheets) overlaid on both sides with a tetrahedrally coordinated silicate network. It has been proposed that brucite sheets, which are formed by two-dimensional condensation, act as incipient templates for subsequent condensation of silicate layers [3,4]. Several reports have shown how ordered inorganic–organic hybrids can be prepared under non-hydrothermal conditions [5–9]. Whilton et al. [8] and Carrado et al. [9] investigated one-step synthesis of

ordered organo functionalized magnesium silicates using series of organoalkoxysilanes with lamellar structures analogous to talc. Although layered magnesium organo silicates (MOSs; synthetic talc) with organic functionalities have been prepared, there have been limited studies on the catalytic activity or other applications of these materials. Faria et al. reported porphyrin iron(III) supported on amino functionalized phyllosilicates (natural and synthetic talc) as a heterogeneous catalyst for oxidation of alkanes and alkenes [10]. Sales et al. have described the application of functionalized synthetic talc for adsorption of heavy metals [11].

Solid base catalysts have emerged as cleaner and atom efficient alternatives toward conventionally used liquid bases for the synthesis of many commercially important products. Commercially, condensation reactions are carried out under homogeneous conditions using NaOH, KOH or a mild base such as 40 (mol%) solution of primary, secondary and tertiary amine. Besides environmental problems, these processes have other drawbacks such as use of hazardous liquid bases like KOH, NaOH or amine, lower product selectivity, separation and post-reaction work-up of spent liquid bases. Amines and imines are well known homogeneous catalysts used for various organic transformations due to their basic functionalities [12,13]. How-

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ever, there need to be used in more than stoichiometric amounts. In view of above, development of new solid base catalysts bearing advantages such as easy handling and separation of catalyst, re-usability of catalyst and minimum corrosion could be of great significance. Molnar and Rac [14] and Shimizu et al. [15] have described the condensation of aldehydes catalyzed by amine immobilized silica materials. 2-Methylpentenal is a commercially important chemical that is used in pharmaceuticals, fragrances, flavors, cosmetics and as an intermediate for the synthesis of various pharmacologically active compounds [16,17]. This is presently synthesized by self-condensation of propanal in the presence of a liquid base in stoichiometric amount. Recently, as-synthesized and activated hydrotalcite samples have been reported as active solid base catalysts for the aldol condensation of propanal [18]. In the present study, we are reporting utilization of MOS as an efficient solid base catalyst for self-condensation of propanal and as well as other aldehydes and ketones.

2. Experimental

2.1. Materials

Tetraethoxyorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTMS), N-[3-(trimethoxysilyl) propyl] ethylenediamine (MSPEA, 80% solution), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) were obtained from Sigma–Aldrich and used as such. Methanol and sodium hydroxide were purchased from s.d. Fine Chemicals, India. The propanal and 2-methylpentenal were purchased from Sigma–Aldrich, USA and used without further purification. Natural talc (NT) was purchased from Associated Soapstone Distribution Co. Pvt. Ltd., Rajasthan.
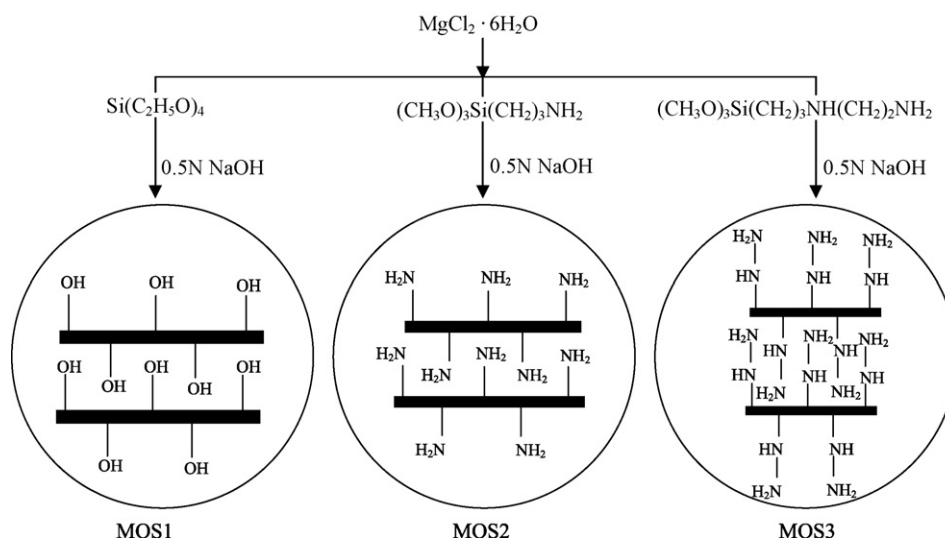
2.2. Catalyst synthesis

$MgCl_2 \cdot 6H_2O$ (8.36 g each in three flasks) was dissolved in 200 mL of methanol, and solutions were stirred at 25 °C. Then,

solution of 11.1 g TEOS (for synthesis of MOS1), 9.8 g APTMS (for synthesis of MOS2) and 15.3 g MSPEA (for synthesis of MOS3) in 50 mL of methanol was separately added drop wise into these flasks. These mixtures formed white suspension. To these mixtures, 0.5 M NaOH solution was slowly added until the pH reached 10.5 with stirring at 25 °C. The obtained suspensions were aged for 1 week at 25 °C, and gels formed were centrifuged, washed with double distilled de-ionized water until a neutral solution was detected. The gels were dried at 65 °C and denoted as MOS1, MOS2 and MOS3. The Si/Mg ratio was maintained at 1.33 in preparation of MOS. The representative scheme for synthesis of MOS is shown in Scheme 1.

2.3. Characterization of catalyst

Powder X-ray diffraction (P-XRD) analysis of MOS was carried out with Philips powder diffractometer X'Pert MPD system using PW3123/00 curved Cu-filtered Cu Kα (λ = 1.54056 Å) radiation with slow scan of $0.3° s^{-1}$. Fourier transform infrared (FT-IR) spectra were measured with Perkin Elmer GX-FTIR using KBr pellet. CHN analysis of MOS was carried out with Perkin Elmer CHNS/O analyzer (Series II, 2400). Thermo gravimetric analysis (TGA) were carried out using Mettler TGA/SDTA 851e equipment in flowing nitrogen (flow rate, 50 mL/min), at a heating rate of 10 °C/min. Morphology of the MOS was determined using scanning electron microscope (Leo Series VP1430, Germany) having silicon detector. MOS samples were coated with gold using sputter coating prior to measurement. Analysis of the samples were carried out at an accelerating voltage of 15 kV. Surface area of MOS was determined from N_2 adsorption data measured at 77 K using Micromeritics, ASAP 2010, USA. The samples were activated at 110 °C for 2 h under vacuum (5×10^{-2} mmHg) prior to N_2 adsorption measurements. The specific surface area of the samples was calculated from N_2 adsorption isotherms according to the Brunauer, Emmett, Teller (BET) method. The CO_2 adsorption–desorption data were obtained by adsorption and desorption of CO_2 at 30 °C.

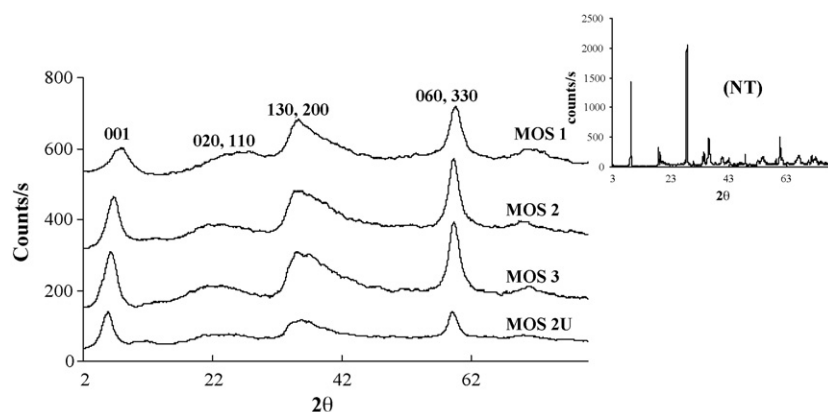Scheme 1. Schematic representation for the synthesis of magnesium organo silicates (MOS).

Fig. 1. P-XRD patterns of magnesium organo silicates (NT, MOS1, MOS2 and MOS3) and used catalyst (MOS2U).

2.4. Self-condensation reaction

The pre-calculated amounts of propanal, catalyst and solvent were taken with 0.01 g of tetradecane as an internal standard in an oven dried double necked round bottom flask for self-condensation of propanal. One neck of flask was fitted with 0.7 m long refluxing condenser with spiral tube and other neck of flask was blocked with silicon rubber septum. The top of the refluxing condenser was closed by a standard size cork. Water at 15 °C was circulated in refluxing condenser continuously during the course of reaction from water chiller at a flow rate of 6 L/min. Flask fitted with refluxing condenser was kept in an oil bath equipped with temperature and agitation speed controlling unit. Reaction was carried out at 100 °C for 10 h. After completion of the reaction, reaction mixture was cooled down to room temperature and was subsequently filtered. The weight of initial reaction mixture and product mixture after reaction was compared to ensure the absence of vapor loss of propanal. The conversion of propanal was calculated by internal standard method. Analysis of product mixture was carried out by gas chromatography (GC) (Shimadzu 17A, Japan) and GC–MS (mass spectrometer, Shimadzu-QP2010, Japan). GC has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The retention time of different compounds was determined by injecting pure compounds into GC column under identical GC conditions. 2-Methylpentenal and 3-hydroxy-2-methylpentanal were observed to be the major products formed in this study. However, formation of 3-pentanone and C_9 products such as 2,4-dimethyl-2,4-heptadienal, 2,4-dimethyl-2-heptenal, ethyl-2-hydroxybutyl propionate were also observed under the studied experimental conditions. The conversion, selectivity and turn over frequency (TOF) were calculated using following equations:

$$\text{conversion}\,(\%) = \frac{\text{moles of propanal reacted}}{\text{moles of propanal fed}} \times 100$$

%selectivity of 2-methylpentenal

$$= \frac{\text{moles of 2-methylpentenal}}{\text{moles of (2-methylpentenal + 3-hydroxy-2-methylpentanal + 3-pentenone + } C_9 \text{ products)}} \times 100$$

TOF

$$= \frac{\text{moles of (2-methylpentenal+3-hydroxy-2-methylpentanal)}}{\text{moles of amine groups in the catalyst} \times \text{time}}$$

Regeneration of the catalyst was carried out by washing the spent catalyst sample with dimethyl sulphoxide (DMSO) five times and dried at 80 °C for 4 h. Repeated experiments were carried out to ensure reproducibility for self-condensation of propanal under identical reaction conditions. The conversions and selectivities were observed to be reproducible within ±5% variation.

3. Results and discussion

3.1. Catalyst characterization

P-XRD reflections of MOS shows broader peaks as compared to natural talc sample (NT), suggesting significant disorder due to the presence of organic moieties in interlayer space (Fig. 1). Basal spacing of (0 0 1) plane for MOS1was observed as 1.1 nm. This value increased to 1.3 and 1.4 nm for organic functionalized MOS2 and MOS3, respectively (Table 1) showing the presence of amine and diamine functionalities in the interlayer space. The intra-layer reflection of (0 6 0) and (3 3 0) planes are characteristic of the 2:1 trioctahedral phyllosilicate structure. These reflections remained unchanged in MOS2 and MOS3 samples indicating that the layered inorganic framework can accommodate a range of organic functionalities without loss of long-range periodicity [1–4]. There was no significant change observed in P-XRD pattern of MOS2U as compared to MOS2, confirming that the structure remained unaltered in the used catalyst.

BET surface area of MOS1, MOS2 and MOS3 (Table 1) was calculated as 189, 3 and 2 m^2/g, respectively. Pore volume of MOS1, MOS2 and MOS3 samples was observed as 0.102, 0.006 and 0.002 cm^3/g, respectively. The observed decrease in surface area and pore volume of MOS2 and MOS3 is due to the

Table 1
Structural and textural properties of studied catalysts

	Catalysts		
	MOS1	MOS2	MOS3
d_{001}-Spacing (nm)	1.1	1.3	1.4
BET surface area (m^2/g)	189	3	2
CO$_2$ adsorption (cm^3/g)	34.4	5.03	5.99
CO$_2$ adsorption (mmol/m^2)	0.008	0.075	0.133
CO$_2$ desorption (cm^3/g)	14.9	0.28	0.17
Pore volume (cm^3/g)	0.102	0.006	0.002
Amine group content (mmol/g)	–	2.5	3.8
SiO$_2$ (%, w/w)	54.3	44.9	35.7
MgO (%, w/w)	17.9	14.8	11.8
Loss on ignition (%, w/w)	19.7	35.2	46
Moisture content (%, w/w)	8.1	5.1	6.5

IR bands assignments

Mg–O stretch	550 cm^{-1}	–NH$_2$	1638, 1561, 1492, 1388, 1344 cm^{-1}
Si–O–Si stretch	1051, 1130 cm^{-1}	Bicarbonate	1411, 1384 cm^{-1}
Si–C stretch	1188 cm^{-1}	–NH$_3^+$	1596 cm^{-1}
O–H stretch	3400–3450 cm^{-1}	MgO–H stretch	3700 cm^{-1}

presence of amine and diamine functionalities in the interlayer space of MOS.

Characteristic framework vibrational modes observed in the FT-IR spectra of all samples were consistent with the proposed talc-like structure (Fig. 2). These included Mg–O stretch (550 cm^{-1}), Si–O–Si stretch within a 2:1 phyllosilicate (1051 cm^{-1}), Si–C stretch (1188 cm^{-1}), O–H stretch (adsorbed water; silanol groups; 3400–3450 cm^{-1}), and Mg–OH (3700 cm^{-1}). Methyl and methylene units presented bands at 2938 cm^{-1}. Bands seen at 1638, 1561, 1492, 1388 and 1344 cm^{-1} in the MOS2 and MOS3 samples suggest the presence of amine groups and amine attached to alkyl chain [1–4].

CHN analysis reveals %C, %H and %N for MOS2 as 11.4, 4.6 and 3.6; for MOS3 as 14.8, 5.6 and 5.3, respectively. The C/N ratio of MOS2 and MOS3 was calculated as 3.6 (theoretical 3.0) and 2.8 (theoretical 2.5), respectively, confirming the complete hydrolysis of all methoxy groups in MOS2 and MOS3. TGA data show initial weight loss of 8.1, 5.1 and 6.5% for MOS1, MOS2 and MOS3, respectively, in the temperature range of 50–120 °C (Fig. 3). The initial weight loss in MOS samples is attributed to the loss of physically adsorbed water from the structure of talc. The weight loss observed at higher temperature range of 120–250 °C may be due to the re-arrangement of grafted silanol, and/or release of strongly bound water on the surface. MOS1 shows higher weight loss in the temperature range of 120–250 °C as compared to MOS2 and MOS3 due to presence of higher number of silanol groups. Above 250 °C, decomposition of amine groups occurs in MOS2 and MOS3 samples. The MOS2 and MOS3 samples showed weight loss in two stages in the temperature range of 250–700 °C. First stage occurs in the temperature range of 250–450 °C, in which 12.3% and 13.1% weight loss for MOS2 and MOS3, respectively, was observed due to the
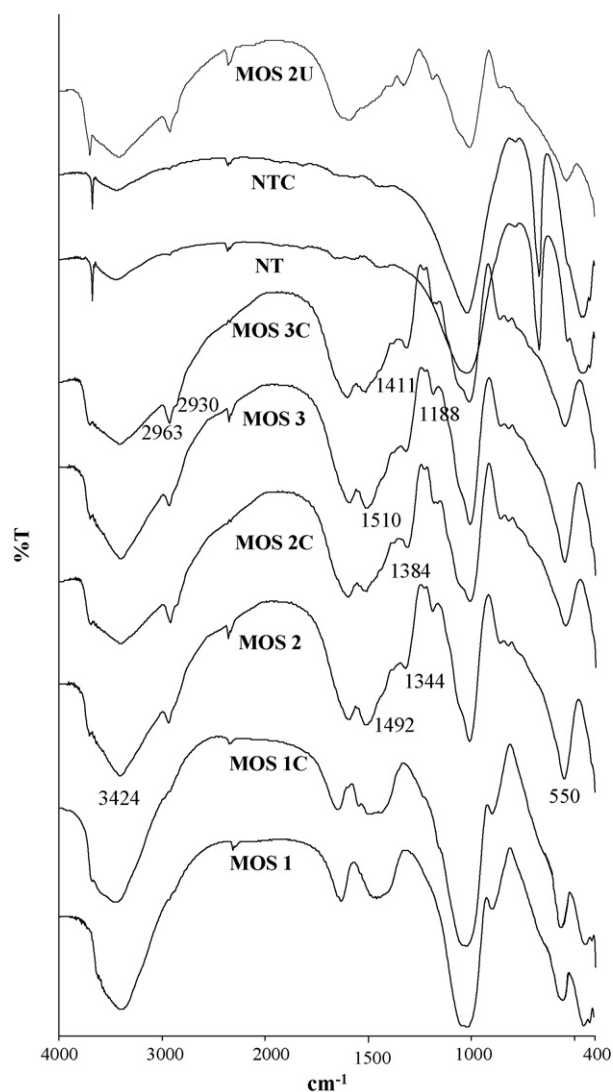

Fig. 2. FT-IR Spectra of natural talc (NT), synthetic talc before (MOS1–3) and after (NTC and MOS1C–3C) CO$_2$ adsorption and used catalyst (MOS2U).
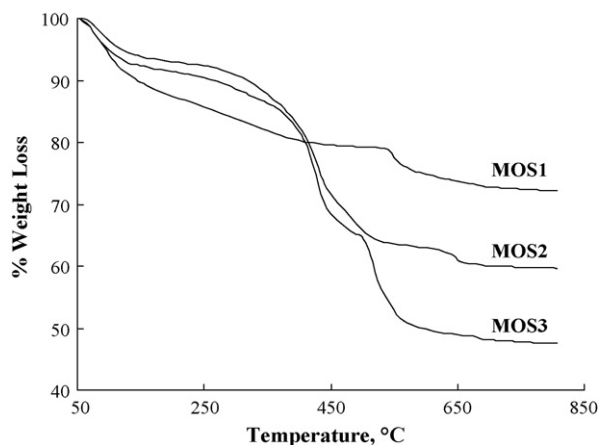

Fig. 3. Thermogravimetric analysis of magnesium organo silicates (MOS1, MOS2 and MOS3).

decomposition of amines. At temperatures above 450 °C, weight loss for MOS2 and MOS3 reached up to 22.6% and 32.4%, respectively, due to increase in the decomposition of amines. The MOS2 and MOS3 were functionalized by [–(CH$_2$)$_3$NH$_2$] and [–(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$], respectively. The higher weight loss in MOS3 as compared to MOS2 samples is attributed to presence of higher organic content or bulkier diamine functional groups. Two steps weight loss was observed in MOS2 and MOS3 sample, due to decomposition of amine [–(CH$_2$)$_3$NH$_2$] and ethylenediamine [–(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$] functionalities in first step and removal of structural hydroxyl groups (i.e., Si–OH and Mg–OH) along with decomposition of amines in the second stage in the temperature range of 550–700 °C. The higher weight loss in MOS3 sample is supported by the amine content data presented in Table 1. The amines content in the MOS2 sample was calculated as 2.5 mmol/g and 3.8 mmol/g for MOS3. The lower weight loss in MOS1 as compared to MOS2 and MOS3 samples was observed due to removal of hydroxyl groups attached to the framework. These data show that the grafted amine species are stable up to 200 °C in nitrogen atmosphere.

The micrographs obtained by SEM shown in Fig. 4 demonstrate the presence of well-formed structure of irregular shapes and sizes. These particles exhibit plate-like morphology, indicating layered structure of these hybrids. The micrographs of MOS2 and MOS3 show separated platelets as compared to MOS1 due to presence of amine and diamine functionalities in MOS2 and MOS3 samples.

3.2. Catalytic activity

To evaluate catalytic activity of MOS1, MOS2 and MOS3 samples, preliminary experiments were performed at 100 °C for self-condensation of propanal in toluene (Table 2). Natural talc (NT) sample showed 32% conversion of propanal. For synthetic talc samples, conversion of propanal was observed to increase with increasing amount of amine functionalities in MOS. For example, 24% conversion of propanal was observed within 10 h at 100 °C using MOS1 as a catalyst which increased up to 65% in amine functionalized MOS2 sample. Furthermore, for diamine functionalized catalyst (MOS3), conversion of propanal increased to 70%. Only 3% conversion of propanal
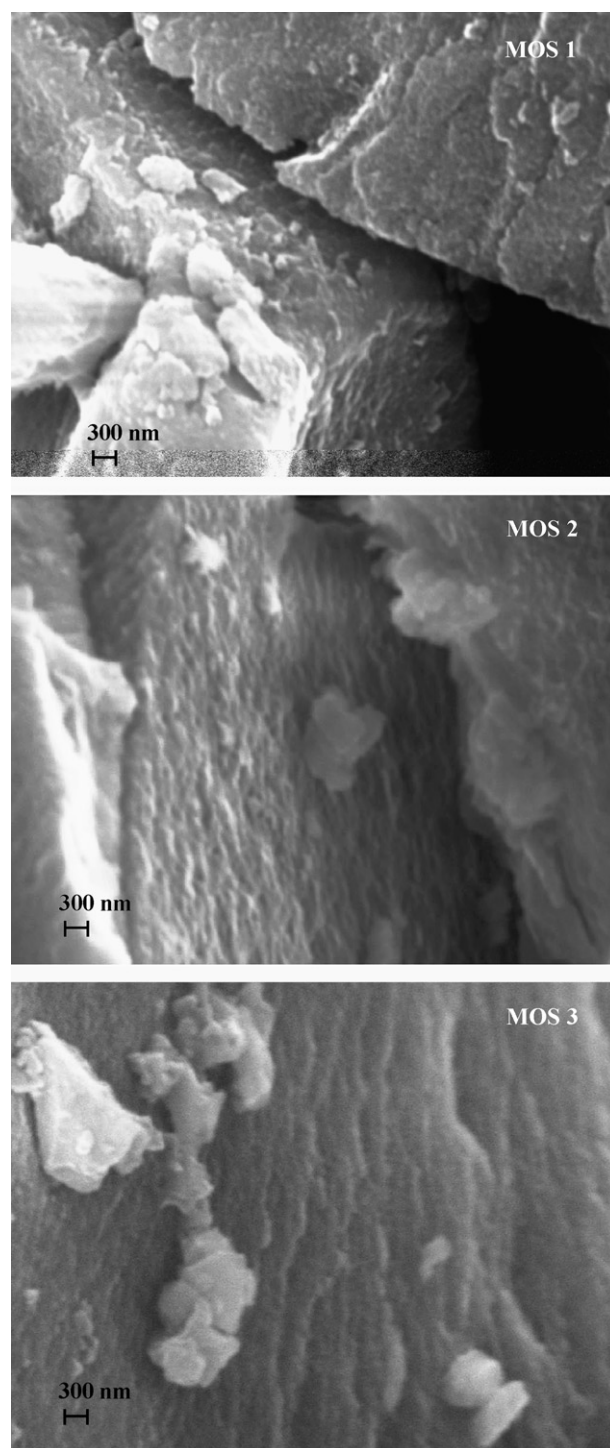

Fig. 4. Scanning electron micrographs of MOS1, MOS2 and MOS3.

was observed by carrying a reaction without catalyst. The basicity of catalyst increased significantly by incorporating amine/diamine functionality in MOS that is resulting into the observed increase in the conversion of propanal. The increase in basicity of catalyst on amine functionlization was further supported by CO$_2$ desorption data (Table 1) measured at 30 °C. Carbon dioxide adsorption–desorption isotherms are given in Fig. 1 (supplementary material). Adsorption of CO$_2$ can occur through physisorption and/or chemisorption on the catalyst sur-

Table 2
Effect of functional groups on conversion and selectivity for self-condensation of propanal[a]

Entry	Catalyst	% Conv	% Selectivity		
			2-Methyl pentenal	3-Hydroxy-2-methyl pentanal	C$_9$ products
1	MOS1	24	98	2	–
2	MOS2	65	95	–	5
3	MOS3	70	82	14	4
4	NT	32	99	–	1
5	Without	4	75	25	–

[a] Reaction conditions: propanal = 1.25 g, catalyst = 0.1 g, temperature = 100 °C, solvent (toluene) = 5 mL, time = 10 h.

face. CO_2 desorption values (14.9 cm^3/g for MOS1, 0.28 cm^3/g for MOS2, 0.17 cm^3/g for MOS3) indicates that 43% of CO_2 is desorbed from MOS1, while only 5.5% and 2.8% of CO_2 gets desorbed from MOS2 and MOS3 at 30 °C, clearly indicating that chemisorbed CO_2 is higher in MOS2 (94.5%) and MOS3 (97.2%) as compared to MOS1 (57%). As CO_2 chemisorption occurs on basic sites of the catalyst, the data clearly shows that the basicity of catalysts increases on introducing amine/diamine functionalities. In the FT-IR spectra of CO_2 adsorbed MOS (Fig. 2), bands in low frequency regions at 1411 and 1384 cm^{-1} assigned to the bicarbonate species appeared in MOS2C and MOS3C. The relative intensities of these two bands vary as moisture is introduced into the system. When carbon dioxide is dry, the band at 1411 cm^{-1} is intense, the band at 1384 cm^{-1} increased gradually as adsorptive became humid. A band at 1596 cm^{-1} appeared and assigned to the formation of NH_3^+ due to adsorption of carbon dioxide on MOS2 and MOS3. The conversion of propanal observed in case of NT as a catalyst could be due to the presence of basic oxides as can be observed from the chemical analysis of NT performed using ICP-AES (60.4% SiO_2, 28.7% MgO, 1.2% Al_2O_3, 0.07% Fe_2O_3, 2.3% CaO, 1.8% Na_2O and 6.13% loss on ignition). The ICP-AES analysis of MOS samples were also carried out to verify whether samples contain any residual sodium or not, results shows presence of 0.0003, 0.0005, 0.0002 wt% of Na in MOS1, MOS2 and MOS3, respectively.
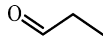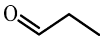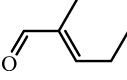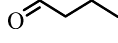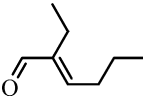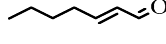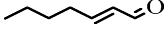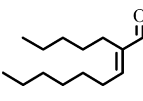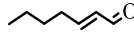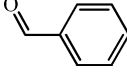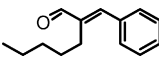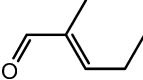
MOS2 was further studied for self as well as cross condensation of aldehydes and ketones (Table 3). MOS2 showed 98% conversion of heptanal with 90% selectivity of 2-pentylnonenal during self-condensation of heptanal. The mass fragmentation

data for all studied reactions are given in Fig. 2 (supplementary material). For self-condensation of ketones, 70% conversion of acetone with 57% selectivity of 2-methyl-2-pentenal was obtained in 10 h reaction time. 84% selectivity of jasminalde-hyde and 16% for 2-pentylnonenal (self-condensation product of 1-heptanal) were observed by condensation of 1-heptanal with benzaldehyde using MOS2. The results presented in Table 3 show that the MOS2 is an active solid base catalyst for self and cross condensation of aldehydes and ketones. Detailed study to evaluate catalytic activity of MOS2 was carried out using propanal as a model reactant.

3.3. Effect of solvent

The catalyst activity data for MOS2 and MOS3 for self-condensation of propanal given in Tables 4 and 5, show that higher conversion and selectivity was observed in polar solvents. For example, conversion of propanal was observed to be 65% with toluene which decreased to 54% with benzene as a solvent for MOS2 as a catalyst (Table 4). Higher selectivity of 2-methylpentenal (95%) was found in toluene as compare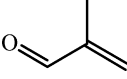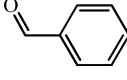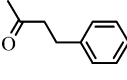d to benzene (91%). Lower conversion of propanal with poor selectivity of 2-methylpentenal was observed in case of hexane, cyclohexane, 1,4-dioxan as solvents. However, selectivity for 3-hydroxy-2-methylpentanal and C_9 products was observed to increase in case of non-polar solvents. The polar solvents such as *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethyl acetamide (DMA) and DMSO showed higher conversion and selectivity for propanal condensation as compared to non-polar solvents under similar reaction conditions. 77% conversion of propanal

Table 3
Condensation of aldehydes and ketones using MOS2 without solvent[a]

Entry	Substrate A	Substrate B	% Conv	Aldol product	% Selectivity of aldol product
1			90		77
2			83		75
3			98		90
4[b]			80		84
5			70		57
6			85		60
7			80		68

[a] Reaction conditions: molar ratio of substrate A to B = 1:1, catalyst = 0.1 g, temperature = 100 °C, time = 10 h.
[b] Molar ratio of substrate A to B = 1:5.

Table 4
Effect of solvent on conversion and selectivity for self-condensation of propanal using MOS2 as a catalyst[a]

| Entry | Solvent | Dielectric constant | % Conv | % Selectivity | | | | TOF (h^{-1}) |
				2-Methyl pentenal	3-Hydroxy-2-methyl pentanal	3-Pentanone	C$_9$ products	
1	Nil	–	90	77	6	3	14	6.5
2	Hexane	1.9	22	42	39	7	12	1.5
3	Cyclohexane	2.0	26	45	40	5	10	2.0
4	1,4-Dioxan	2.1	32	35	62	–	3	2.7
5	Carbon tetrachloride	2.2	41	75	18	2	5	3.3
6	Benzene	2.3	54	91	3	–	6	4.4
7	Toluene	2.4	65	95	–	5		5.3
8	*N,N*-dimethyl formamide	38	77	82	–	6	12	5.4
9	*N,N*-dimethyl acetamide	37.8	78	83	–	3	14	5.6
10	Dimethyl sulphoxide	47.2	86	95	–	2	3	7.0

[a] Reaction conditions: propanal = 1.25 g, catalyst = 0.1 g, temperature = 100 °C, solvent = 5 mL, time = 10 h.

Table 5
Effect of solvent on conversion and selectivity for self-condensation of propanal using MOS3 as a catalyst[a]

| Entry | Solvent | Dielectric constant | % Conv | % Selectivity | | | | TOF (h^{-1}) |
				2-Methyl pentenal	3-Hydroxy-2-methyl pentanal	3-Pentanone	C$_9$ products	
1	Nil	–	84	65	10	6	19	3.6
2	Hexane	1.9	48	40	47	3	10	2.4
3	Toluene	2.4	70	82	14	–	4	3.8
4	Carbon tetrachloride	2.24	52	81	12	2	5	2.7
5	*N,N*-dimethyl acetamide	37.8	75	94	–	6	–	3.9
6	Dimethyl sulphoxide	47.2	80	98	–	2	–	4.2

[a] Reaction conditions: propanal = 1.25 g, catalyst = 0.1 g, temperature = 100 °C, solvent = 5 mL, time = 10 h.
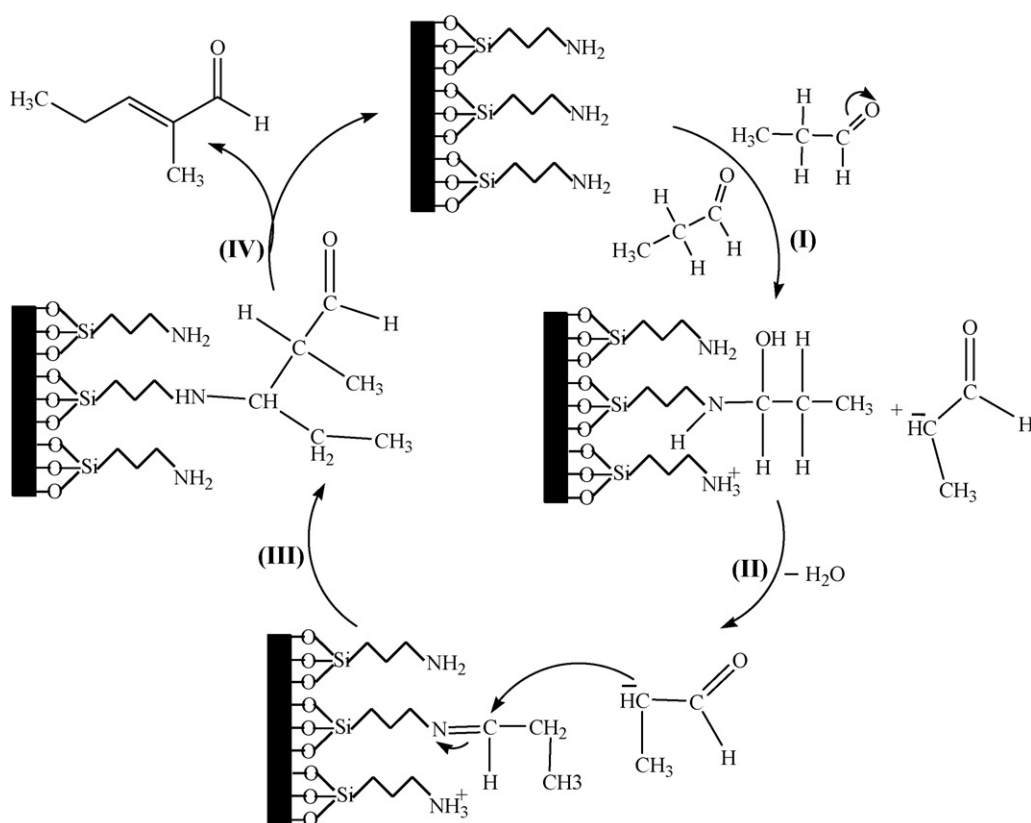
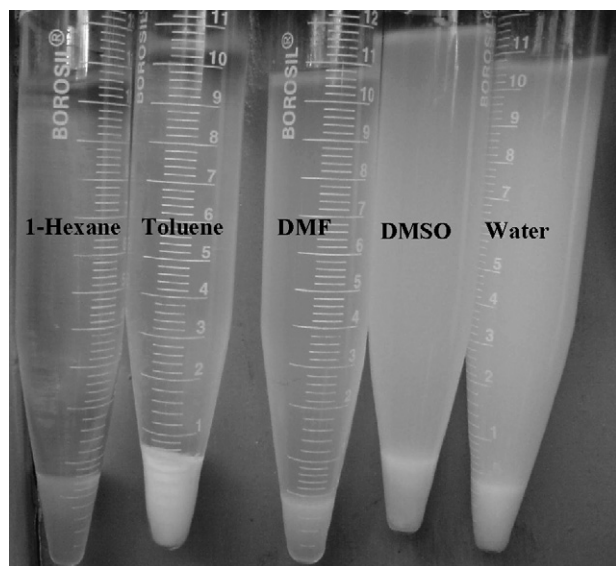Scheme 2. Proposed reaction mechanism for self-condensation of propanal.

Fig. 5. Swelling of MOS2 in non-polar and polar solvents after 6 h.

with 82% selectivity of 2-methylpentenal was observed in case of DMF. Conversion of propanal increased up to 86% with 95% selectivity of 2-methylpentenal with DMSO as a solvent. Self-condensation of propanal was also carried out in the absence of solvent. Higher propanal conversion (90%) with lower selectivity of 2-methylpentenal (77%) was observed in solvent free conditions as compared to the reaction conditions in the presence of toluene or DMSO. Lower selectivity of 2-methylpentenal under solvent free conditions is due to formation of C_9 products (2,4-dimethyheptadienal, ethyl-2-hydroxybutyl propionate) by further condensation of self-condensed product with another propanal molecule. For MOS3 catalyst also, polar solvents showed better conversion and selectivity for self-condensation of propanal (Table 5). Higher activity of catalysts in polar solvents can be attributed to stabilization of intermediates (Scheme 2) and transfer of protons as compared to non-polar solvents. Moreover, higher degree of swelling of the catalyst was observed in polar solvents as compared to non-polar solvents (Fig. 5). The experiments were carried out for swelling of MOS2 in different solvents, such as 1-hexane, toluene, dimethyl formamide, dimethyl sulphoxide and water. The higher swelling of MOS 2 was observed in water followed by dimethyl sulphoxide, dimethyl formamide, toluene and 1-hexene. Due to higher

swelling of catalyst in polar solvents, the catalytic activity gets increased by enhanced participation of active basic sites present on the surface as well as in the interlayers. Calculated TOF's for MOS2 and MOS3 catalyzed condensation of propanal were also observed to increase with increasing dielectric constant values of the studied solvents.

Further detailed study for optimization of reaction parameters for self-condensation of propanal including the effect of, solvent to reactant molar ratio, amount of catalyst and temperature was carried out using MOS2 as a catalyst in the DMSO.

3.4. Effect of solvent to reactant ratio

Effect of solvent to reactant molar ratio on propanal condensation was studied by varying the moles of solvent at 100 °C. At lower ratio (0.5), higher conversion (91%) of propanal was observed (Table 6). The conversion of propanal decreased to 86% with increase in the ratio to 3. However, on further increase in the ratio to 10, the conversion of propanal decreases significantly up to 72%. Lower conversion of propanal at higher solvent to reactant ratio could be a purely kinetic effect resulting from lower concentration of reactant. Another possible reason for the decrease in conversion at higher solvent to reactant ratio may be due to the blockage of active sites present on the surface of catalyst. This is also supported by the results observed for condensation of propanal in the absence of solvent (Table 4, entry 1) and at lower solvent to reactant ratio (Table 6, entries 1 and 2). The TOF values were also observed to decrease on increasing this ratio.

3.5. Effect of catalyst amount

The effect of catalyst amount on conversion of propanal and selectivity of 2-methylpentenal was studied by varying the amount of catalyst (Table 7). At lower catalyst amount (12.5 mg), only 40% conversion of propanal with 60% selectivity of 2-methylpentenal was observed. The total number of active basic sites is lower at lower amount of catalyst and hence lower catalytic activity was observed. On increasing the catalyst amount to 25 mg, conversion of propanal increased up to 75% with 77% selectivity of 2-methylpentenal. Significant changes in conversion of propanal were not observed in the range of 62.5–150 mg catalyst, however, selectivity of 2-methylpentenal

Table 6

Effect of solvent (DMSO) to reactant molar ratio on conversion and selectivity for self-condensation of propanal using MOS2 as a catalyst[a]

| Entry | Solvent/reactant molar ratio | % Conv | % Selectivity | | | TOF (h^{-1}) |
			2-Methyl pentenal	3-Pentanone	C_9 products	
1	0.5	91	96	1	3	7.5
2	1.0	89	97	1	2	7.4
3	1.5	86	98	1	1	7.2
4	2.0	85	98	1	1	7.1
5	3.0	86	95	2	3	7.0
6	4	80	97	2	1	6.7
7	6	78	98	2	–	6.5
8	10	72	98	2	–	6.1

[a] Reaction conditions: propanal = 1.25 g, catalyst = 0.1 g, temperature = 100 °C, time = 10 h.

Table 7

Effect of amount of catalyst on conversion and selectivity for self-condensation of propanal using MOS2 as a catalyst[a]

Entry	Catalyst (mg)	% Conv	% Selectivity				TOF (h^{-1})
			2-Methyl pentenal	3-Hydroxy-2-methyl pentanal	3-Pentanone	C$_9$ products	
1	12.5	40	60	37	3	–	26.8
2	15.5	51	72	16	2	10	24.8
3	25	75	77	8	4	11	22.0
4	50	82	83	–	5	12	11.7
5	62.5	85	88	–	4	8	10.3
6	100	86	95	–	2	3	7.0
7	150	87	95	–	2	3	4.6
8	250	92	93	–	3	4	3.0

[a] Reaction conditions: propanal = 1.25 g, solvent (DMSO) = 5 mL, temperature = 100 °C, time = 10 h.

was observed to increase significantly. On further increase in the catalyst amount to 250 mg, conversion of propanal was observed to increase to 92% with decrease in selectivity of 2-methypentenal to 93%. The calculated TOF values decreased from 26.8 to 3 with increase in catalyst amount from 12.5 to 250 mg. At higher catalyst amount, total number of available active basic sites is higher and the probability for interaction of these sites with reactant molecule would increase, which could have led to higher conversion and selectivity for condensation reaction.

3.6. Effect of reaction temperature

Effect of reaction temperature (50–120 °C) on conversion and selectivity of 2-methylpentenal was studied at 21.5 mmol concentration of propanal, 0.1 g catalyst, 5 mL solvent (DMSO; Table 8). Conversion of propanal was observed to increase on increasing reaction temperature. For example at 50 °C, slow reaction with only 15% conversion of propanal was observed in 10 h. The conversion of propanal was found to be 78% and 91% at reaction temperatures of 80 and 120 °C, respectively. On the other hand, selectivity of 2-methylpentenal was observed to decrease on increasing the reaction temperature due to further condensation of propanal with aldol product at higher reaction temperature. Strong adsorption of propanal molecule on active sites of catalyst at lower temperature is responsible for low activity of the catalyst for self-condensation of propanal [19]. The calculated turnover frequency increases from 1.3 to 7.5 on increasing the reaction temperature from 50 to 120 °C.

Fig. 6. Conversion of propanal as a function of reaction time using MOS2 and MOS3 as catalyst.

3.7. Kinetics and reusability of the catalyst

Changes in the concentration of propanal with respect to reaction time was studied using MOS2 and MOS3 under optimum reaction conditions, i.e., solvent to propanal molar ratio 3.0, propanal to catalyst weight ratio 12.5 at 100 °C. Calculated conversion data from concentration of propanal was found to increase regularly up to 7 h followed by slow increase in the conversion (Fig. 6). The values of the rate constant were calculated from the plot of $\ln(-dN_p/dt)$ (on Y-axis) vs. $\ln(N_p)$ (on X-axis); where N_p = mole of propanal. The values of rate constant were calculated as 0.29 M^{-1} h^{-1} for MOS2 and 0.21 M^{-1} h^{-1} for MOS3. The rate constant data for MOS2 and MOS3 catalyst samples indicate that the MOS2 catalyzed self-condensation of

Table 8

Effect of temperature (T) on conversion and selectivity for self-condensation of propanal using MOS2 as a catalyst[a]

Entry	T (°C)	% Conv	% Selectivity			TOF (h^{-1})
			2-Methylpentenal	3-Pentanone	C$_9$ products	
1	50	15	100	–	–	1.3
2	70	41	100	–	–	3.5
3	80	78	100	–	–	6.7
4	90	80	99	–	1	6.8
5	100	86	95	2	3	7.0
6	120	91	96	–	4	7.5

[a] Reaction conditions: propanal = 1.25 g, catalyst = 0.1 g, solvent (DMSO) = 5 mL, time = 10 h.

Table 9
Reusability of catalyst[a]

Cycles	% Conv	% Selectivity		
		2-Methylpentenal	3-Pentanone	C_9 products
1	86	95	2	3
2	86	95	2	3
3	85	95	2	3
4	80	94	3	3

[a] Reaction conditions: propanal = 1.25 g, solvent (DMSO) = 5 mL, temperature = 100 °C, time = 10 h.

propanal is faster than that of MOS3. The second order reaction with respect to reactant was observed for MOS2 and MOS3 catalyzed condensation of propanal.

The re-usability of catalyst was studied under identical reaction conditions. Conversion and selectivity were observed to slightly decrease after three cycles, which could be ascribed to handling loss of catalyst (Table 9). P-XRD pattern and FT-IR spectrum of the used catalyst (MOS2U) also supported that the structure of MOS2 remained unaltered after three cycles (Figs. 1 and 2).

3.8. Reaction mechanism

The proposed reaction mechanism for self condensation of propanal is shown in Scheme 2. In the first step, intermediate species are formed by attack of one propanal molecule on amino group of the catalyst. The resulted intermediate species react with anion of second propanal molecule to produce corresponding C=N imine species in second step [20]. The proton transfer from C=N imine species takes place in third step for the formation of an unstable intermediate called as carbinolamine. The transfer of proton in third step also depends on nature of solvent. Polar solvents assist for rapid proton transfer, results higher conversion and selectivity of desired product. Desorption of 2-methylpentenal from carbinolamine takes place in fourth step.

4. Conclusions

MOS with amine and diamine functionalities were synthesized and characterized by P-XRD, FT-IR, CHNS analyzer, surface area measurements, SEM and used as solid base catalysts for condensation of aldehydes and ketones. The conversion of propanal was observed to increase with increase in the basicity of catalyst using toluene as a solvent. Polar solvents showed higher conversion and selectivity as compared to non-polar solvents for amine/diamine functionalized MOS for self-condensation of propanal. 86% conversion of propanal with 95% selectivity of 2-methylpentenal was observed in case of DMSO as a solvent and MOS2 as catalyst. Higher conversion of propanal (91%) was observed at lower solvent to reactant molar ratio (0.5). The rate constants determined from kinetic experiments were 0.29 M^{-1} h^{-1} (MOS2) and 0.21 M^{-1} h^{-1} (MOS3) at optimized reaction conditions. The catalyst was recycled up to three times for self-condensation of propanal.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.landurbplan.2007.07.001.

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